

# Organometallic cluster complexes with face-capping arene ligands VII<sup>1</sup> Nucleophilic substitution of fluoride in a facially coordinated arene ligand

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## Abstract

Reaction of *p*-fluoro- $\alpha$ -methylstyrene with  $[(\eta\text{-C}_5\text{H}_5)\text{Co}(\eta\text{-C}_6\text{Me}_6)]$  leads to the cluster complex  $[(\eta\text{-C}_5\text{H}_5)\text{Co}]_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}p\text{-fluoro-}\alpha\text{-methylstyrene})$  **1b**. Nucleophilic substitution of fluoride by  $\text{H}^-$  or  $\text{Ph}^-$  takes place when **1b** is treated with  $\text{LiHBEt}_3$  or  $\text{PhLi}$ .

**Keywords:** Arene clusters; Nucleophilic substitution; Cyclopentadienyl cobalt

## 1. Introduction

The reactivity of arene ligands in mononuclear transition metal complexes has been studied in considerable detail [2]. It is well known that the chemical properties of a metal coordinated arene nucleus (and also of its substituents) are substantially different from those of the free ligand. A chemically very useful application has been the strong activation of benzene towards nucleophilic attack by the chromium tricarbonyl moiety [3]. In contrast to mononuclear systems, only little is known about the reactions of arenes which are coordinated to a metal cluster [4,5]. The few studies in this area show that benzene also reacts as an electrophile when coordinated to a metal carbonyl cluster in the terminal ( $\eta^6$ ) or face-capping ( $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ ) bonding mode. For example, carbanions ( $\text{RLi}$ ,  $\text{R} = \text{Me}$ ,  $\text{Ph}$ ) add in the *exo* position to the benzene ligands in  $[\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_6)]$  or  $[(\text{CO})_3\text{Os}]_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$  to give anionic cluster complexes with terminal 1,2,4,5- $\eta$ -cyclohexa-1,4-diene [6] or bridging 1-5- $\eta$ -cyclohexadienyl ligands [7] respectively. However, genuine nucleophilic substitution reactions ( $\text{S}_{\text{N}}\text{Ar}$ ) *via* carbanion addition followed by hydride abstraction have so far been restricted to the systems with terminally bound arene ligands [7,8].

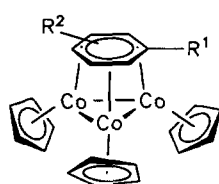
As a part of our studies of the organometallic  $\mu$ -arene cluster complexes of the type  $[(\eta\text{-C}_5\text{H}_5)\text{Co}]_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-arene})$  (arene = alkyl-, alkenylbenzene) **1** [4,9] we became interested in the electrophilic and nucleophilic reactivity of **1**. Since, owing to synthetic difficulties, only a limited range of essentially non-functional arenes is available as bridging ligands in **1** [10] one of our goals was to introduce chemical functionality at the stage of the cluster coordinated arenes. Unfortunately the complexes **1** turned out to be rather unreactive [11b]. We felt that fluoroarenes should be better substrates for nucleophilic substitutions because of the much better properties of the fluoride ion as a leaving group, and the possible activation of the arene compared to a hydrogen substituent. However, in earlier synthetic attempts the cluster complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Co}]_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-fluorostyrene})$  **1a** could only be prepared in very low yield. Preferentially, C–H bond activation of the vinyl groups occurred, which led to the formation of the  $\mu$ -alkyne clusters  $[\text{H}_2\{(\eta\text{-C}_5\text{H}_5)\text{Co}\}_3\text{-}\{\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}(fluorophenyl)ethyne}\}]$  [12]. Here, we now give a preliminary account of the synthesis, molecular structure and some nucleophilic substitution reactions of  $[(\eta\text{-C}_5\text{H}_5)\text{Co}]_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}p\text{-fluoro-}\alpha\text{-methylstyrene})$  **1b**.

## 2. Results and discussion

Reaction of *p*-fluoro- $\alpha$ -methylstyrene with  $[(\eta\text{-C}_5\text{H}_5)\text{Co}(\eta\text{-C}_6\text{Me}_6)]$  [13] in *thf* at room temperature

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<sup>1</sup> Dedicated to Professor Max Herberhold on the occasion of his 60th birthday. For Part VI of this series, see Ref. [1].



	R <sup>1</sup>	R <sup>2</sup>
<b>1a</b>	C(H)=CH <sub>2</sub>	<i>o</i> -, <i>m</i> -, <i>p</i> -F
<b>1b</b>	C(Me)=CH <sub>2</sub>	<i>p</i> -F
<b>1c</b>	C(Me)=CH <sub>2</sub>	H
<b>1d</b>	C(Me)=CH <sub>2</sub>	<i>p</i> -Ph

gave complex **1b** in about 50% yield [14]. Owing to decomposition on attempted chromatography, separation from hexamethylbenzene by fractional crystallisation from *n*-hexane at room temperature was very tedious and accompanied by substantial product loss. However, for synthetic studies the crude product can be used with success. Spectroscopic data [15] for **1b** are in complete agreement with the molecular structure observed in the solid state [16] (Fig. 1). As in all structurally characterised derivatives of **1**, a  $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$  coordination geometry of the essentially planar arene ligand is attained. The structural features of the  $\mu_3$ -arene ligand resemble those previously reported for other complexes of this type [1,4,9,11]. In particular, there is some alternation of the endocyclic carbon–carbon bond lengths, the bonds on top of the cobalt atoms being somewhat shorter (mean  $d_{\text{CC}} = 1.418 \text{ \AA}$ ) than those between the cobalt atoms (mean  $d_{\text{CC}} = 1.444 \text{ \AA}$ ). As predicted by theory [17] the substituents on the  $\mu_3$ -arene are displaced from the ligand plane away from the metal cluster (C7 by 0.44 Å, F1 by 0.55 Å). A small distortion around C1 which involves the endocyclic carbon–carbon and the carbon–cobalt bonds can be attributed to the influence of the sterically demanding isopropenyl substituent.

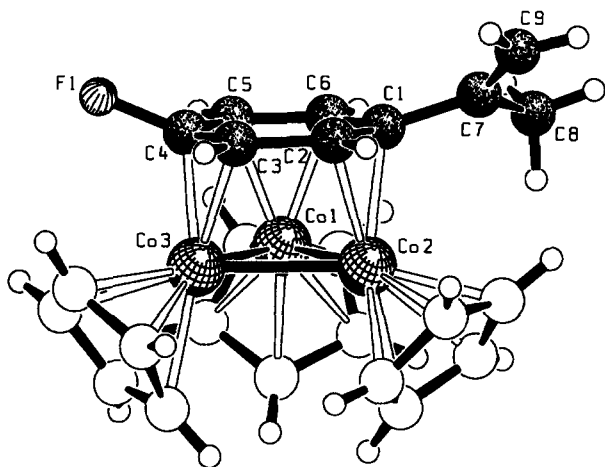


Fig. 1. Molecular structure of **1b**. Selected bond distances (Å) with standard deviations in parentheses: Co(1)–Co(2), 2.484(1); Co(1)–Co(3), 2.488(1); Co(2)–Co(3), 2.499(1); Co(1)–C(5), 2.027(6); Co(1)–C(6), 2.016(5); Co(2)–C(1), 2.060(6); Co(2)–C(2), 2.023(6); Co(3)–C(3), 2.029(6); Co(3)–C(4), 1.976(6); C(1)–C(2) 1.434(7); C(1)–C(6), 1.465(8); C(2)–C(3), 1.435(8); C(3)–C(4), 1.413(8); C(4)–C(5), 1.433(8); C(5)–C(6), 1.407(8); C(1)–C(7), 1.481(8); C(7)–C(8), 1.488(9); C(7)–C(9), 1.322(10), C(4)–F(1), 1.382(6).

The NMR spectroscopic properties of **1b** (notably the high field shift of the <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F resonances of the  $\mu_3$ -fluoroarene ligand) are in line with those of related derivatives [11,12,18]. In solution a fluxional process involving rotation of the arene ligand on top of the metal cluster is apparent from the temperature dependence of the <sup>1</sup>H NMR spectra. Low temperature spectra are in accord with a static structure with a  $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$  coordination of the arene.

After treatment of **1a** with one equivalent of LiHBEt<sub>3</sub>, followed by chromatographic workup on deactivated alumina, the known [11b] cluster complex [(( $\eta\text{-C}_5\text{H}_5$ )Co)<sub>3</sub>( $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}\alpha$ -methylstyrene)] **1c** was isolated in 30% yield [19]. Likewise, the *para*-phenyl-substituted derivative **1d** was obtained in 34% yield from the reaction of **1a** and phenyl lithium [19]. In an experiment carried out under identical conditions, no substitution was observed when free *p*-fluoro- $\alpha$ -methylstyrene was treated with phenyl lithium. Complex **1c** shows resonances due to an uncomplexed phenyl group in the <sup>1</sup>H and <sup>13</sup>C NMR spectra [20], along with the high field resonances [ $\delta(^1\text{H}) \sim 4.5$ ,  $\delta(^{13}\text{C}) = 30\text{--}45$ ] typical for the  $\mu_3$ -arene moiety. A broadened resonance is observed for the cyclopentadienyl protons at room temperature. This signal sharpens on warming of the sample to 330 K and splits into a poorly resolved 2:1 pattern on cooling to 250 K, in accord with a hindered rotation of the arene relative to the tricobalt cluster. The <sup>19</sup>F spectrum is silent.

Substitution of halide by carbanions was reported previously for chromium tricarbonyl complexes of halobenzenes [21a]. In these cases the nucleophile reversibly adds to the  $\eta$ -arene at each of the ring carbons (probably except *para* to the halogen) in the first step under kinetic control. However, elimination of halide occurs from the *ipso* addition product only, resulting in purely *ipso* substitution [21b]. We presume a similar mechanism for the S<sub>N</sub>Ar reactions of the  $\mu_3$ -fluoroarene in **1b**. Our results indicate that the enhancement of nucleophilicity, imposed to the  $\mu_3$ -arene by the [( $\eta\text{-C}_5\text{H}_5$ )Co]<sub>3</sub> cluster, is considerably less than that caused by second- and third-row metal carbonyl clusters. This may be taken as a reflection of the better electron withdrawing capabilities of the metal carbonyl fragments. In addition, the presence of good fluoride acceptors (BEt<sub>3</sub> and Li<sup>+</sup>) is expected to enhance the ease of the reaction in the former case.

## Acknowledgements

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- [14] A mixture of 400 mg (1.4 mmol) of  $[(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{C}_6\text{Me}_6)]$  and 120 mg (0.9 mmol) of *p*-fluoro- $\alpha$ -methylstyrene in 40 ml of thf was stirred at room temperature for 10 h. Solvent was removed from the brown solution under vacuum and the residue extracted with *n*-hexane. The crude product (130 mg of a black microcrystalline conglomerate of **1b** and  $\text{C}_6\text{Me}_6$ , about 85% **1b**) crystallised from the filtrate after reduction of the volume to 10–15 ml (46% yield based on Co).
- [15]  $^1\text{H}$  NMR (200 MHz, in  $\text{C}_6\text{D}_6$ ):  $\delta = 1.56$  (d, 3H,  $\text{CH}_3$ ), 4.47 (m, br, 4H, arene-H), 4.61 (s, br, 5H, 1Cp), 4.68 (s, br, 11H, 2Cp + alkene-H), 5.09 (s, br, 1H, alkene-H); (320 K):  $\delta = 1.56$  (d, 3H,  $\text{CH}_3$ ), 4.52–4.36 (m, (AB) $_2$ , 4H, arene-H), 4.63 (s, 15H, 3Cp), 4.69 (s, br, 1H, alkene-H), 5.09 (s, br, 1H, alkene-H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (50 MHz, in  $\text{C}_6\text{D}_6$ ):  $\delta = 21.9$  ( $\text{CH}_3$ ), 31 (br,  $\mu$ -arene), 36.3 (br,  $\mu$ -arene), 58.1 (br,  $\mu$ -arene), 84.0 (br, Cp), 105.3 ( $\beta$ - $\text{CH}_2$ ), 149.1 (C- $\alpha$ ).  $^{19}\text{F}\{^1\text{H}\}$  NMR (84.3 MHz, in  $\text{C}_6\text{D}_6$ ):  $\delta = -148.6$ . EI-MS (70 eV)  $m/z = 508$  (25%,  $\text{M}^+$ ), 372 (15,  $[(\text{C}_5\text{H}_5)_3\text{Co}]^+$ ), 370 (100,  $[(\text{C}_5\text{H}_5)_3\text{Co}]_3 - 2\text{H}^+$ ), 310 (12), 247 (14,  $[(\text{C}_5\text{H}_5)_2\text{Co}]_2 - \text{H}^+$ ), 189 (47,  $[(\text{C}_5\text{H}_5)_2\text{Co}]^+$ ), 124 (18,  $[(\text{C}_5\text{H}_5)\text{Co}]^+$ ).
- [16] *Crystal Structure Analysis of 1b*: monoclinic, space group  $P2_1/c$ ,  $a = 15.790(4)$ ,  $b = 7.620(2)$ ,  $c = 17.575(5)$  Å,  $\beta = 112.78(2)^\circ$ ,  $V = 1949.7(9)$  Å $^3$ ,  $Z = 4$ . Intensity data were collected at ambient temperature using a Syntex R3 four circle diffractometer (Mo K $\alpha$  radiation, graphite monochromator.  $\omega$ -scan.  $3 \leq 2\theta \leq 50^\circ$ .  $hkl$ -range  $0 \leq h \leq 18$ ,  $0 \leq k \leq 9$ ,  $-20 \leq l \leq 19$ ). Reflections measured: 3442, independent 3442; empirical absorption correction. The structure was solved with direct methods. Refinement: full matrix least squares on  $F^2$ . All non-hydrogen atoms anisotropic, olefinic H-atoms of the bridging ligand localised in difference Fourier syntheses and refined with isotropic displacement parameters, all other H-atoms inserted in calculated positions.  $R = 0.055$  (2444 reflections with  $F_o \geq 4\sigma(F_o)$ ),  $wR2 = 0.112$  (on  $F^2$ , all reflections),  $w = [\sigma^2(F_o^2) + (0.0329P)^2 + 3.05P]^{-1}$ ,  $P = [\max(F_o^2, 0) + 2F_c^2]/3$ ,  $\text{Goof} = 1.119$ . All calculations were performed using SHELXLS-86 (G.M. Sheldrick, *Acta Crystallogr. Sect. A*, **46** (1990) 467) and SHELXL-93 (G.M. Sheldrick, Universität Göttingen, 1993). Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-404925, the names of the authors, and the journal citation.
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- [19] *Reactions of 1b with nucleophiles*: a solution of the nucleophile was added to an *n*-hexane solution (30 ml) of crude **1b** (containing 15%  $\text{C}_6\text{Me}_6$ ) at room temperature. The mixture was stirred overnight, reduced in volume under vacuum and then chromatographed on deactivated (5%  $\text{H}_2\text{O}$ ) alumina. Hexamethylbenzene was washed from the column with *n*-hexane. The organometallic product is then eluted with toluene. **1c**: from 0.2 ml of a 1 M solution of  $\text{Li}[\text{HBEt}_3]$  in thf and 90 mg (0.18 mmol) of **1b** 30 mg (30%) of **1c** was obtained.  $^1\text{H}$  NMR spectra were identical to those of an authentic sample [11b] **1d**: 0.15 ml of a 2 M solution of phenyl lithium in cyclohexane–diethyl ether and 105 mg (0.21 mmol) of **1b** gave 40 mg (34%) of **1d** as a brown powder.
- [20]  $^1\text{H}$ -NMR (200 MHz, in  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 2.09$  (s, 3H,  $\text{CH}_3$ ), 4.60 (br, 1H,  $\mu_3$ -arene), 4.82 (s, br, 18H,  $\eta\text{-C}_5\text{H}_5 + \mu_3$ -arene), 5.01 (s, 1H, H(C- $\beta$ )), 5.29 (s, 1H, H(C- $\beta$ )), 6.69 (d, 1H, Ph), 7.3 (br, 1H, Ph), 7.7 (m, 3H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR (50 MHz, in toluene- $d_6$ ):  $\delta = 22.0$  ( $\text{CH}_3$ ), 30.3 ( $\mu_3$ -arene), 42.1 ( $\mu_3$ -arene), 44.2 ( $\mu_3$ -arene), 80.8 ( $\eta\text{-C}_5\text{H}_5$ ), 111.2 (C- $\beta$ ), 120.1 (Ph), 134.1 (Ph or C- $\alpha$ ), 144.6 (Ph or C- $\alpha$ ), 148.0 (Ph), 151.8 (Ph).
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